New chemical vapor delivery systems for surface cleaning

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Keywords: Surface Cleaning, Hydrogen Peroxide, Ammonia, Iso-propanol, Chemical Vapor Delivery

Introduction

Conventional aqueous wet cleaning methods in semiconductor manufacturing are facing tremendous challenges, with decreasing line widths and high aspect ratio features on the order of a few nanometers. Water and other liquids have surface tensions that frequently prevent complete penetration into nanometer-sized trenches and vias now being fabricated on semiconductor wafers and other substrates. This problem is accentuated by the fact that particle sizes leading to “Killer” defects are now on the order of 10 nm or less. Nanometer-sized particles can adhere to a surface with a relatively strong force of over a million times its weight. An effective cleaning technique for submicron particle removal will require complete penetration of the device features to surround and dislodge particles, but at the same time not damage the features or etch the surface.

Novel “dry” cleaning methods are now being sought, where the term “dry” refers to gas phase or vapor chemistries. Many current “dry” techniques rely on highly reactive and corrosive chemistries (e.g., HF, F2, O3 and Cl2 gases) to form volatile by-products that may later be removed in vacuum. These chemistries are compatible with only a limited number of applications. In most instances, problems still remain for removal of nanometer-sized particles, organic films, and non-volatile molecular species. Nanometer-sized particles are reaching the realm of molecular contamination. Molecular contaminants arising from hydrocarbons or plastics can range in size from 0.2-10 nm. Thus, large molecular contaminants such as organic molecules are similar in size to metallic atom or metal oxide clusters. Wafer and other critical surface cleaning must consider factors on the molecular level such as:

- Elemental composition of the surface.
- Elemental composition of the particles.
- Intermolecular bonding and other forces that hold particles in place.

Our approach entails the development of vapor phase chemistries, where chemical mixtures are delivered and removed in the gas phase. The physical and chemical properties of multi-component chemical mixtures can lead to removal of nanometer-sized particles as well as molecular contaminants. Here, chemical vapor compositions may be tailored toward the quenching of adhesive forces.

The design and delivery of new vapor phase chemistries has been the initial focus of this work. Vital to the success of any vapor phase chemistry is delivery of consistent compositions, temperature and pressure. Limited success obtained by early workers in this area can be attributed to a lack of process control or the inability to deliver high concentrations of low vapor phase chemistries in multi-component systems. This study demonstrates the viability of a new membrane technology for the precise delivery of multi-component chemistries. To date, work has focused on vapor phase delivery of H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O, NH\textsubscript{3}/H\textsubscript{2}O and Isopropanol/H\textsubscript{2}O mixtures.
Membrane Technology

In this study, a novel membrane delivery system which incorporates temperature, pressure, and flow rate control as well as chemical precursor purification has been employed. The system adds controlled amounts of vapor chemistry to any carrier gas. The unit may operate in atmospheric and vacuum pressures, and uses liquid solution sources. The device utilizes a hydrophilic membrane that excludes organic and metal contaminants from entering the vapor stream. Liquid sources from the membrane unit do not come into direct contact with the vacuum system or reaction environment.

Chemical Delivery System

A carrier gas flows into the membrane assembly where liquid chemistries diffuse across a membrane into the carrier gas (Figure 1). The temperature of the carrier gas is then measured and fed back to a temperature controller to adjust the chemistry concentration level. Internal pressure control maintains independence from variations in downstream process pressures allowing operation into atmospheric and vacuum pressure environments.

The chemical vapor delivery system consists of a non-porous membrane that excludes particles, micro-droplets, volatile gases, and other opposite charged species from being transferred to the carrier gas and ensures only vapor is added. The membrane is highly selective, preventing most carrier gases from crossing over into the source (Figure 2). Selectivity of up to a million to one water molecules over nitrogen has been found. Organic and metal contaminants in the liquid source cannot permeate across the membrane or enter the carrier gas stream, resulting in a chemical vapor saturated product that is consistent and pure.

The carrier gas is saturated based on the temperature at the gas/liquid interface, providing accurate delivery of chemical vapor. With the addition of a back pressure regulation device, low vapor pressure gases can be delivered into sub-atmospheric processes.

Figure 1. Membrane in tube form. Liquid diffuses in a radial direction.
Hydrogen Peroxide Vapor Delivery

Extreme difficulty lies in the delivery of vapor phase hydrogen peroxide. Liquid hydrogen peroxide H2O2 is commonly used as 30% H2O2/H2O solutions. The inherent low vapor pressure of H2O2 versus H2O in these mixtures leads to delivery of 8 parts hydrogen peroxide per 1000 parts water at 20°C. Many published reports exist on the use of hydrogen peroxide vapor in semiconductor processes, however, in actuality, very little hydrogen peroxide is delivered to the process.

Bubblers, and other crude delivery devices are highly unstable with respect to mass transfer rates. As the vapor is drawn off by vacuum or carrier gas, water is preferentially removed and the H2O2 concentration increases. In addition, evaporative cooling takes place which, when combined with changes in concentration, leads to highly variable mass transfer rates. In the case where temperature is controlled, variable liquid concentration levels still lead to unstable delivery concentrations. An example of this instability is shown in Figure 3.
A new technology that is capable of generating and delivering stable concentrations of H2O2 vapor has been developed (Figure 4). Pervaporation devices are used in series, where pre-loading a carrier gas first with water and then flowing through a pervaporator filled with H2O2/H2O mix enables a controlled H2O2/H2O ratio to be delivered to a process. Here, pre-humidification with water vapor ensures maintenance of the liquid source concentration, which not only ensures process control but also has safety ramifications.

Initial studies show that water vapor may be added to the upstream carrier gas in order to keep the liquid hydrogen peroxide solution concentration constant. However, if too little humidification is added to the upstream carrier gas, the hydrogen peroxide liquid concentration increases. If too much humidification is
added upstream, the hydrogen peroxide liquid concentration decreases. Figure 5 demonstrates this crossover effect.

Figure 5. Crossover effect of hydrogen peroxide liquid concentration with respect to upstream humification levels.

The preload on the carrier gas was varied from 0% to 110% rH. Initially, as the preload was increased, the amount of H2O2 picked up by the carrier gas increased to peak around 70%. This point was slightly below the transition point for water vapor reversing flow from out of the solution to back into the solution.

Figure 6 shows stable delivery of a ~30% H2O2 solution at 40°C. The average H₂O₂ concentration was 700ppm with a standard deviation of 16ppm. For the solution, the beginning concentration average was 33.4% and the final concentration average was 33.2%. This demonstrates the ability to control the hydrogen peroxide mass transfer rate while maintaining a relatively stable liquid solution concentration.
Figure 6. H$_2$O$_2$ Output at 40°C with 30% Solution.

The output of a ~70% H$_2$O$_2$ solution held at 40°C is shown in Figure 7. The average H$_2$O$_2$ concentration was 2583 ppm with a standard deviation of 23 ppm. For the solution, the beginning concentration average was 69.1% and the final concentration average was 69.9%.
Dilute Ammonia/Water Vapor Delivery

Oxide and silicon loss during cleaning is no longer acceptable, therefore dilute chemistries are being sought. Dilute solutions of ammonia/water delivered from the vapor phase is a promising candidate for emerging applications. Ammonia mass transfer through a membrane delivery system was examined.

Data in Figure 8 show dilute ammonia concentrations delivered from a liquid 0.5% NH4OH/Water solution at 30°C. Mass transfer rates can be adjusted by varying flow rate.

In a subsequent test, ammonia concentration in the liquid solution was varied to study the effects on the delivered concentration. Results show in Figure 9 that higher vapor phase concentrations may be obtained by adjusting solution concentration. However, these results demonstrate that the membrane acts as an attenuation device, as the delivered concentrations are less than would be expected from a liquid solution with the use of a bubbler.
Figure 8. Concentration of delivered ammonia starting from a 0.5% NH$_4$OH solution.

Figure 9. Concentration of ammonia delivered at various source solution concentrations.
Isopropanol/Water Vapor Delivery

Vapor iso-propanol/water solutions show promise in the removal of residual organic compounds from surfaces as well as stain-free drying. Initial studies were undertaken to examine delivery of this two-component mixture. Iso-propanol concentrations in a water solution were varied in order to look at changes in delivered iso-propanol concentrations. Results demonstrate the viability of the new membrane technology for delivery of a wide range of iso-propanol concentration.

Figure 10. Concentration of IPA vapor delivered at various solution concentrations.

Alternatively, Pure IPA vapor may be delivered from an anhydrous solution. Figure 11 shows IPA vapor delivery with the data in linearized form. Linearization of data is important when considering a method of system control. Simple controllers only have the capability to apply linear functions to execute tasks such as correlating the concentration of chemical vapor in a stream based on the flow rate of carrier gas. A successful linear correlation was found for the variable flow rate experiments by plotting vapor concentration versus inverse flow rate.
Figure 11. Delivery of Anhydrous Iso-propanol at variable flow rates.

Conclusion

Controlled delivery of H2O2/water, NH3/water, IPA/water and anhydrous IPA have been demonstrated. The availability of these chemistries in stable, controlled vapor form provides a wide range of potential cleaning formulations for advanced structures and metal surfaces. Future work in this area will involve studies with collaborators on specific problems inherent to sub-20nm processes in development.